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Supplementary information

Surface reactivity of non-hydrolytic silicophosphate xerogels: A simple way to Brønsted or Lewis acid sites on porous supports

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Experimental

Synthesis of parent xerogels

SiP. The parent silicophosphate xerogel was prepared under conditions optimized to give the maximum surface area.[1] In a typical reaction, $OP(OSiMe_3)_3$ (TTP) was added dropwise to a stirred solution of $Si(OAc)_4$ (molar ratio 4:3) in toluene to obtain a clear colorless gel (eq. 1). The gel was aged at 80 °C for one week and then dried under vacuum for two days providing an opaque xerogel (**SiP**). Characterization and spectral analysis data of **SiP** were same as reported previously.[1]

IR (**SiP**, KBr, cm^{-1}) ν : 490 w, 651 w (ν SiC_3), 765 w (ρ_s $SiCH_3$), 853 vs (ρ_{as} $SiCH_3$), 1021 vs (ρ CH_3), 1050 vs (ν Si−O−P), 1111 vs (ν P−O−Si), 1230, 1258 vs (δ_s $SiCH_3$) 1300 sh (ν P=O), 1374 w (δ_s CH_3), 1420 w (δ_{as} CH_3), 1540 s, 1721 w (ν_{as} C=O), 1768 s (ν_{as} C=O), 2907 vw (ν_s CH_3), 2964 w (ν_{as} CH_3).

^{13}C CPMAS NMR (**SiP**, ppm) δ : −1.3 ($POSiCH_3$), 16.3 (CH_3COO bident), 20.4 (CH_3COO unident), 165.5 (CH_3COO unident), 190.6 (CH_3COO bident).

^{29}Si CPMAS NMR (**SiP**, ppm) δ : 23.6 ($POSiMe_3$), −112 (SiO_4), −162 (SiO_5), −195 (SiO_6), −214 (SiO_6).

^{31}P MAS NMR (**SiP**, ppm) δ : −45 ($P(OSi)_4$).

BET: 568 m^2 g^{-1}.

$$3\ Si(OAc)_4 + 4\ OP(OSiMe_3)_3 \rightarrow Si_3P_4O_{16} + 12\ CH_3C(O)OSiMe_3 \quad (1)$$

$$(AcO)_3Si\text{-}(CH_2)_2\text{-}Si(OAc)_3 + 2\ OP(OSiMe_3)_3 \rightarrow OPO_3Si(CH_2)_2SiO_3PO + 6\ AcOSiMe_3 \quad (2)$$

SiC2SiP. Similarly, the synthesis of hybrid silicophosphate xerogel was adopted from our previous work.[2] $OP(OSiMe_3)_3$ was added dropwise to a stirred solution of $(AcO)_3SiCH_2CH_2Si(OAc)_3$ in toluene (molar ratio 2:1). After the addition was complete, stirring was stopped and the reaction mixture was kept at 80 °C for one week. The reaction mixture provided a milky rigid gel overnight (eq. 2). The reaction was stopped after one week and dried under vacuum affording opaque xerogel (**SiC2SiP**). Characterization and spectral analysis data of **SiC2SiP** were same as reported previously.[2]

IR (**SiC2SiP**, KBr, cm^{-1}) *v* : ν 490 m, 608 vw, 639 vw (*v* SiC_3), 763 m (ρ_s $SiCH_3$), 790 sh, 851 m (ρ_{as} $SiCH_3$), 1018 vs (ν Si−O−P), 1175 m, 1231 w, 1259 m (δ_s $SiCH_3$), 1313 s (*v* P=O), 1374 vw (δ_s CH_3), 1406 vw, 1601 vw, 1754 m (ν_{as} CH3COO unident), 2906 vw (ν_s CH_3), 2963 w (ν_{as} CH_3).

^{13}C CPMAS NMR (**SiC2SiP**, ppm) δ : 1.2 (POSi*C*H_3), 3.7 shoulder (Si*C*H_2*C*H_2Si), 22.3 (*C*H_3COO unident), 170.6 (CH_3*C*OO unident).

^{29}Si MAS NMR (**SiC2SiP**, ppm) δ : 26 ($POSiMe_3$), −65 ($O_3SiCH_2CH_2SiO_3$).

^{31}P MAS NMR (**SiC2SiP**, ppm) δ : −37 ($O{=}P(OSi)_3$).

BET: 703 m^2 g^{-1}.

Chemical modification of silicophosphate xerogel surfaces.

Modification with H_2O. Characterization and analyses of **SiPH1** xerogel.

IR (**SiPH1**, KBr, cm^{-1}) *v* : 505 m, 610 vw, 686 vw, 762 m (ρ_s $SiCH_3$), 851 vs (ρ_{as} $SiCH_3$), 1077 vs (*v* Si−O−P), 1095 vs (*v* P−O−Si), 1259 s (δ_s $SiCH_3$), 1376 vw (δ_s CH_3), 1419 vw (δ_{as} CH_3), 1548 w (ν_{as} COO bident), 1716 w (ν_{as} COO unident), 1768 w (ν_{as} COO unident), 1656 w (δ OH), 2910 vw (ν_s CH_3), 2965 w (ν_{as} CH_3).

^{13}C CPMAS NMR (**SiPH1**, ppm) δ : −3.9 (POSi*C*H_3), 12.5 (*C*H_3COO bident), 17.6 (*C*H_3COO unident), 163.0 (CH_3*C*OO unident), 186.7 (CH_3*C*OO bident).

^{29}Si CPMAS NMR (**SiPH1**, ppm) δ : 18.3 ($POSiMe_3$), −119 (SiO_4), −201 (SiO_6), −219 (SiO_6).

^{31}P MAS NMR (**SiPH1**, ppm) δ : −49 ($P(OSi)_4$), −40 ($P(OH)(OSi)_3$).

TG/DSC (air, 5 K min^{-1}): weight loss at 1000 °C: 37.7 %.

BET: 279 m^2 g^{-1}.

Characterization and analyses of **SiPH3** xerogel.

IR (**SiPH3**, KBr, cm^{-1}) *v* : 495 m, 607 vw, 675 vw, 761 m (ρ_s $SiCH_3$), 853 vs (ρ_{as} $SiCH_3$), 1070 vs (v Si−O−P), 1261 s (δ_s $SiCH_3$), 1419 w (δ_{as} CH_3), 1669 w (δ OH), 2910 vw (v_s CH_3), 2966 w (v_{as} CH_3).

TG/DSC (air, 5 K min^{-1}): weight loss at 1000 °C: 46.4 %.

BET: nonporous

Characterization and analyses of **SiC2SiPH1** xerogel.

IR (**SiC2SiPH1**, KBr, cm^{-1}) *v* : 496 m, 611 vw, 677 vw, 764 m (ρ_s $SiCH_3$), 851 s (ρ_{as} $SiCH_3$), 1025 vs (v Si−O−P), 1258 s (δ_s $SiCH_3$), 1413 w (δ_{as} CH_3), 1665 w (δ OH), 2900 vw (v_s CH_3), 2965 w (v_{as} CH_3).

^{13}C CPMAS NMR (**SiC2SiPH1**, ppm) δ : 0.6 (Si*C*H_2*C*H_2Si + POSi*C*H_3).

^{29}Si CPMAS NMR (**SiC2SiPH1**, ppm) δ : 26.5 ($POSiMe_3$), −67 ($CSiO_3$).

^{31}P MAS NMR (**SiC2SiPH1**, ppm) δ : −22 ($O{=}P(OH)(OSi)_2$), −9 ($O{=}P(OH)_2(OSi)$).

TG/DSC (air, 5 K min^{-1}): weight loss at 1000 °C: 28.1 %.

BET: 42 m^2 g^{-1}.

Modification with hexamethyldisiloxane. Characterization and analyses of **SiC2SiPHMDSO** xerogel.

IR (**SiC2SiPHMDSO**, KBr, cm^{-1}) *v* : 190 m, 607 vw, 644 vw, 762 m (ρ_s $SiCH_3$), 850 s (ρ_{as} $SiCH_3$), 1032 vs (v Si−O−P), 1175 vw, 1258 s (δ_s $SiCH_3$), 1408 w (δ_{as} CH_3), 2906 vw (v_s CH_3), 2962 w (v_{as} CH_3).

^{29}Si CPMAS NMR (**SiC2SiPHMDSO**, ppm) δ : 24.0 (PO*Si*Me_3), 14.2 (SiO*Si*Me_3) −66 (C*Si*O_3).

^{31}P MAS NMR (**SiC2SiPHMDSO**, ppm) δ : −30 ($O{=}P(OSi)_3$.

TG/DSC (air, 5 K min^{-1}): weight loss at 1000 °C: 35.3 %.

BET: 338 m^2 g^{-1}.

Modification with benzyltrichlorosilane. Characterization and analyses of **SiPPhCH2Si** xerogel.

IR (**SiPPhCH2Si**, KBr, cm^{-1}) *v* : 501 s, 650 w, 698 w, 762 m (ρ_s $SiCH_3$), 852 s (ρ_{as} $SiCH_3$), 1035 vs (v Si−O−P), 1124 vs (v P−O−Si), 1258 s (δ_s $SiCH_3$), 1373 w (δ_s CH_3), 1424 w (δ_{as} CH_3), 1541 w (v_{as} COO bident), 1719 w (v_{as} COO unident), 1765 w (v_{as} COO unident), 2907 vw (v_s CH_3), 2963 w (v_{as} CH_3), 3032 vw (v_s CH ar.), 3061 vw (v_{as} CH ar.).

^{13}C CPMAS NMR (**SiPPhCH2Si**, ppm) δ : –4.5 (POSi*C*H$_3$), 12.8 (*C*H$_3$COO bident), 17.3 (*C*H$_3$COO unident + C$_6$H$_5$*C*H$_2$Si), 124.5 (*C*$_6$H$_5$CH$_2$Si), 163.3 (CH$_3$*C*OO unident), 188.0 (CH$_3$*C*OO bident).

^{29}Si CPMAS NMR (**SiPPhCH2Si**, ppm) δ : 27.0 (POSiMe$_3$), –41.5 (C$_6$H$_5$CH$_2$Si(Cl)O$_2$), –66 (C$_6$H$_5$CH$_2$SiO$_3$),–113 (SiO$_4$), –196 (SiO$_6$), –214 (SiO$_6$).

^{31}P MAS NMR (**SiPPhCH2Si**, ppm) δ : –49 (P(OSi)$_4$.

TG/DSC (air, 5 K min^{-1}): weight loss at 1000 °C: 32.6 %.

BET: 385 m^2 g^{-1}.

Results

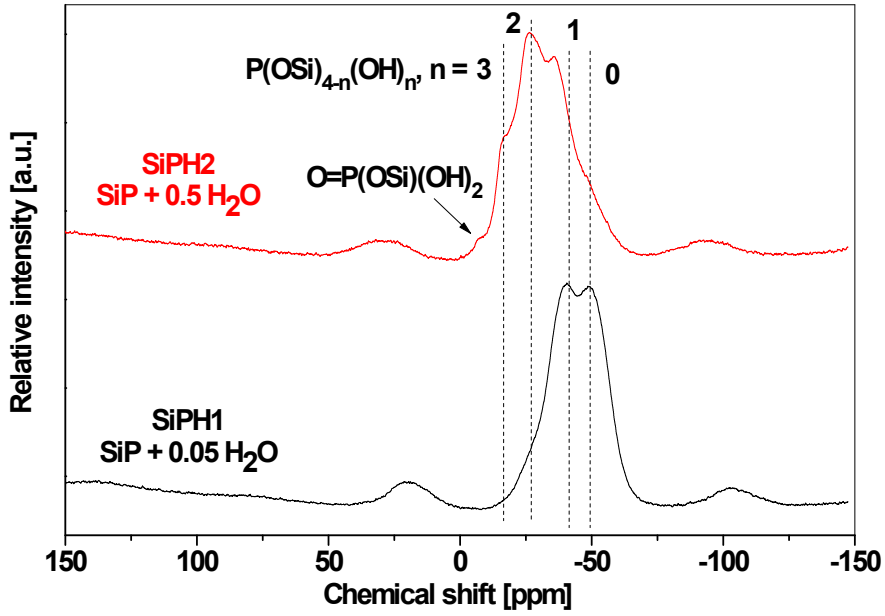

Fig. 1S: Comparison of ^{31}P MAS NMR spectra of SiPH1 and SiPH2 samples.

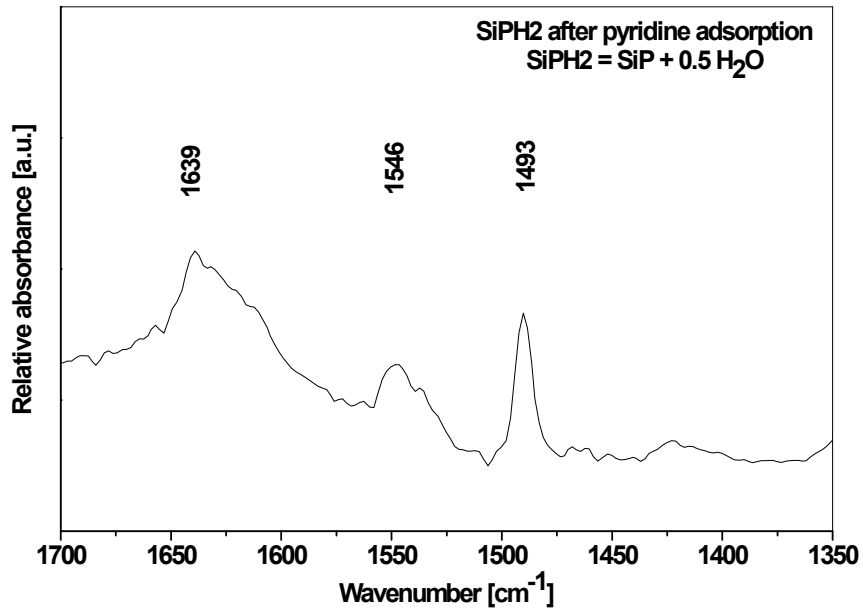

Fig. 2S: IR spectrum of SiPH2 xerogel after pyridine adsorption.

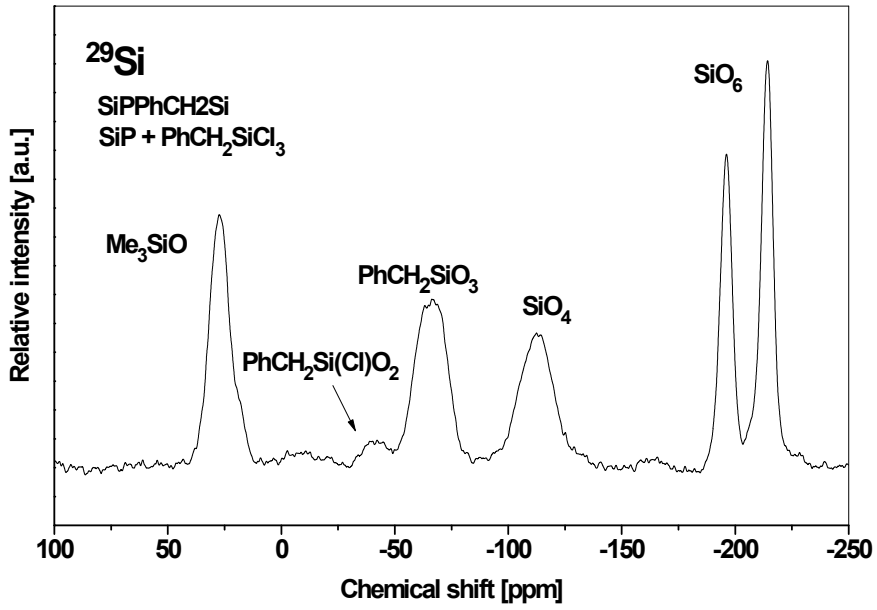

Fig. 3S: ^{29}Si CPMAS NMR spectrum of SiPPhCH2Si xerogel.

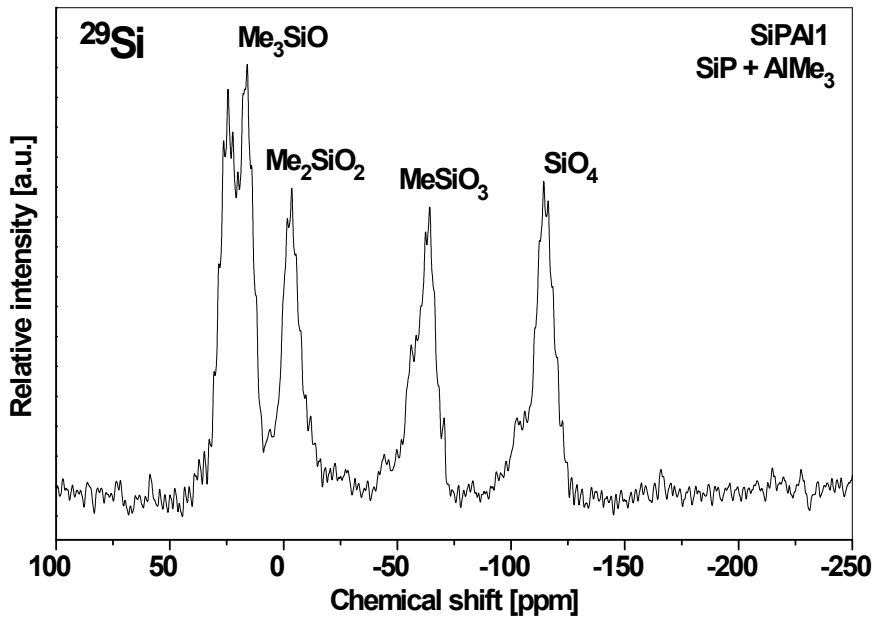

Fig. 4S: ^{29}Si CPMAS NMR spectrum of SiPAl1 xerogel.

References

(1) Styskalik, A.; Skoda, D.; Moravec, Z.; Abbott, J. G.; Barnes, C. E.; Pinkas, J. *Microporous Mesoporous Mater.* **2014**, *197*, 204–212.

(2) Styskalik, A.; Skoda, D.; Moravec, Z.; Babiak, M.; Barnes, C. E.; Pinkas, J. *J. Mater. Chem. A* **2015**, *3* (14), 7477–7487.